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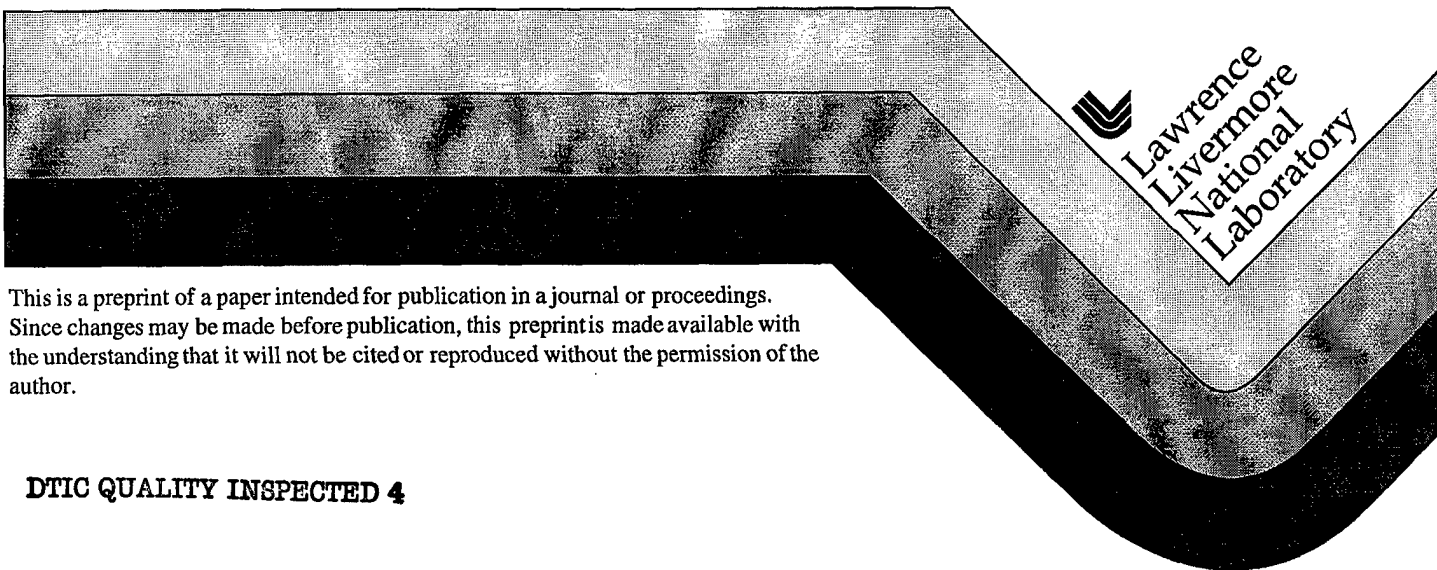
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Decarburization of Uranium Via Electron Beam Processing

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For many commercial and military applications, the successive Vacuum Induction Melting of uranium metal in graphite crucibles results in a product which is out of specification in carbon. The current recovery method involves dissolution of the metal in acid and chemical purification. This is both expensive and generates mixed waste. A study was undertaken at Lawrence Livermore National Laboratory to investigate the feasibility of reducing the carbon content of uranium metal using electron beam techniques. Results will be presented on the rate and extent of carbon removal as a function of various operating parameters.

Introduction

Uranium metal, because of its high density (19 g/cc) finds use in a variety of applications, both military and commercial. Its major use up until about 1995 was as a high-density material for armor penetrating bullets. Smaller amounts of the metal are used for commercial applications such as counterweights on extended wing surfaces of aircraft, shielding for medical isotopes, etc. Uranium metal, both depleted material and that enriched in the fissile 235 isotope, is vacuum induction melted in graphite crucibles and poured into metal ingots for further thermo-mechanical processing to produce a final part. During the melting process, uranium, being highly reactive in the liquid state, picks up from 20-50 ppm carbon from the graphite crucible. This limits the amount of metal that can be reverted before exceeding the 100-200 ppm carbon specification limit for most alloys. Current practice for depleted uranium that is out of specification in carbon, is to burn the material to a non-reactive oxide, then mix into a cement block and bury at an approved disposal site.

Out of specification enriched uranium, due both to regulatory requirements and its high dollar value, is recycled by dissolving in Nitric acid, purifying via a solvent extraction step, conversion of the purified uranyl nitrate hexahydrate to uranium hexafluoride and reducing the hexafluoride to tetrafluoride and then back to metal. Each processing step

creates hazardous, radioactive or mixed waste, which must then be disposed of in compliance with current environmental, safety and health regulations. All of this has become much more costly in recent years and is expected to become even more so in the future.

Various schemes for reducing the carbon in uranium alloys have been reported in the literature. Hafnium additions during vacuum induction melting of pure uranium apparently form low density, insoluble hafnium carbides, which float and are prevented from entering the cast ingot. The ingot, however, is then left with some small amount of hafnium as an alloying element. Further, this mechanism doesn't seem to work with U-6Nb or some of the other common uranium alloys.

A 1969 patent (British patent #1,173,014 to Hugh R. Smith) claims to have demonstrated reduction of carbon in uranium alloys by introducing oxygen over an electron beam heated bath of liquid uranium. The mechanism for this being some form of the equilibrium reaction $2UC + O_2 \rightarrow 2U + 2CO$. Other literature citations indicate that hydrogen may also be used as the reacting species via the reaction $UC + 2H_2 \rightarrow U + CH_4$, although the thermodynamics for this do not appear favorable.

Current Work

In late 1997, a proof of principle experiment was conducted at Lawrence Livermore National Laboratory to investigate the feasibility of removing carbon from uranium by introducing oxygen over an electron beam heated melt. Under the operating conditions used, a modest reduction in carbon from 350 to 300 ppm was achieved, and based upon this result, a project was initiated to quantify carbon reduction as functions of various operating parameters.

All experiments were done using uranium depleted in the fissile ^{235}U isotope. As the main use of this technology would probably be for uranium enriched in the ^{235}U isotope though, it was decided to operate batch experiments with a total mass of not more than 10 kg of uranium so as to simulate operating conditions under mass limits for enriched uranium imposed by nuclear criticality. With this limitation in mind, experiments were designed around a 3.8" diameter, 2" long cylindrical disk weighing ~7 kg. A quantity of disks having a target carbon level of 300-500 ppm was obtained from a commercial uranium supplier. The disks were manufactured by vacuum induction melting uranium metal and casting into 4" diameter cylindrical molds. The resulting ingots were machined to final diameter and cut into disks. The initial carbon level averaged 300 ppm.

The experimental arrangement used is shown in Figure 1. An existing uranium qualified vacuum furnace having a 250 kW electron beam gun was used for these experiments. A 3.8" I.D. water cooled copper crucible capable of safely dissipating over 70 kW of input EB power was designed and constructed. Oxygen was introduced via a .030" I.D. tantalum tube positioned on top of the crucible and bent down at the end to direct the oxygen stream toward the melt surface, approximately .5" below the top of the crucible. A residual gas analyzer was used to monitor partial pressures of all reaction species, although this proved to be of limited quantitative value at the higher operating pressures due to saturation of the signal above about 5×10^{-5} torr.

A series of 16 separate experiments was performed in which carbon depletion was measured as functions of the following operating parameters:

- Power inputs of 35 and 70 kW
- Up to 120 minutes reaction times
- High and low power densities
- Oxygen bleeds up to 9 cc/sec

Experimental Results

Results of the 16 experiments performed to date are shown in the following table:

Expt. Number	Power - kW		Time min	O2 bleed cc/min	Beam D. - in.		Carbon - ppm		Carbon % change	Melt loss grams
	35	70			1	2	Initial	Final		
1	x		60	low	x		304	264	13	208
2	x		60	520	x		308	216	30	54
3	x		60	520	x		308	231	25	21
4	x		60	520		x	306	221	28	18
5	x		60	55		x	299	257	14	18
6	x		60	0	x		320	317	1	242
7	x		120	520	x		315	187	41	162
8	x		30	520	x		303	247	18	101
9		x	15	0		x	289	288	0	69
10		x	14	305		x	313	249	20	10
11		x	60	~140		x	273	237	13	17
12		x	60	388		x	311	234	25	412
13		x	30	388		x	310	260	16	393
14		x	60	0		x	313	276	12	11
15		x	120	388		x	305	134	56	341
16		x	120	220		x	310	127	59	248

Carbon was measured using standard LECO combustion analysis techniques. Reported values were the average of three solid, 0.8 gram samples cut from each disk before and after each experiment.

Above about 2000°C, uranium carbide has a somewhat higher vapor pressure than uranium. To insure that carbon depletion was not simply due to preferential evaporation of the uranium carbide, three experiments were run with no oxygen bleed. Note that experiments 6 and 9 run at 35 kW showed essentially no change in the carbon level, but that the hotter, 70 kW experiment number 14 did show a 12% carbon reduction. If this reduction in carbon is in fact due to evaporation of uranium carbide, this result can be used to enhance the overall kinetics of the process. The benefits of operating hotter to enhance UC evaporation must be balanced, however, with the resulting increase in evaporative losses of uranium at the higher operating power.

Uranium is a highly reactive metal, and it was feared that introducing oxygen directly over the liquid would result in a heavy uranium oxide slag build up on the melt surface. Instead, what was observed was a light oxide dross covering around 50% of the melt surface at the higher oxygen bleeds. The amount of dross did not increase with time, indicating that the process achieves some form of steady-state equilibrium. One possible mechanism for this observation is the reduction of UO_2 to a more volatile sub-oxide under the influence of the intense heat of the electron beam, and the subsequent volatilization of the sub-oxide. A second possibility is that the oxide is reacting with the carbides via the reaction $2\text{UC} + \text{UO}_2 \rightarrow 3\text{U} + 2\text{CO}$. For this reaction, the free energy change becomes negative above 3000°C. The reaction is possible then at high temperature, and as the CO formed is immediately removed in vacuum, the equilibrium for this reaction would tend to shift to the right, again increasing the reaction probability.

Free energy calculations, while a good indication of the probability of a reaction mechanism, say nothing about kinetics. While the reaction is heterogeneous, involving both liquid and gaseous species, and is certainly not in equilibrium, for simplicity it was assumed that the overall reaction for decarburization is $2\text{UC} + \text{O}_2 \rightarrow 2\text{U} + 2\text{CO}$. This reaction has a standard state free energy change at the estimated pool temperature of around 2000°C of $\Delta G = -95$ kcal. With an excess of oxygen, and at high vacuum where evolved CO is immediately removed from the system, the reaction is certainly thermodynamically favored. From chemical kinetics, a simple reaction of this type would be second order in UC and first order in oxygen, and would be expected to follow an overall third order rate equation of the form $k\Theta = 1/C - 1/C_0$. Here, k is a reaction constant, C_0 is the initial carbon concentration and C is the carbon concentration at time Θ . For this set of experiments, however, with an excess of oxygen, it was expected that the reaction would be zero order in oxygen, and the overall reaction would be second

order. Upon fitting the experimental data obtained at 35 kW to the various rate equations, a best fit was obtained with the third order expression as shown in Figure 2. Using this plot, a required reaction time may then be determined for the degree of decarburization desired.

The required oxygen flow rate for these experiments was estimated by assuming a reasonable value for the mass of uranium which would be in the liquid state at the anticipated power levels, and then calculating the amount of uranium carbide within that liquid mass available for reaction. From this, the stoichiometric amount of oxygen required for complete reaction was calculated to be around 16 cc/min for a 1-hour experiment at 70 kW. Actually, oxygen flow rates up to 520 cc/min were used to account for the non-equilibrium nature of the experiments. In Figure 3, Oxygen flow is plotted against the percent reduction in carbon to show the dependence of reaction rate with oxygen bleed. As pointed out in the preceding section, this rate dependence on oxygen flow with such an excess of oxygen was not expected.

The rate of carbon reduction did not appear to be a strong function of input power density over the density range explored. An optimized system could probably be operated at lower power densities where evaporative losses could be minimized.

Overall, these results look very promising for the development of a process to decarburize uranium metal. A 59% reduction in carbon has been achieved in this first series of 16 experiments, and it is expected that process optimization expected during the current year will lead to a process which can be transferred to production facilities in the near future.

Discussion

Thermodynamically, the reaction $2\text{UC} + \text{O}_2 \rightarrow 2\text{U} + 2\text{CO}$ has a high negative free energy of formation, $\Delta G = -75$ kcal, so it should be possible to decarburize uranium using a variety of conventional liquid metal processing techniques. The main process requirement lies in utilizing a heat source that exposes dissolved carbides to the melt surface where it may combine with the oxygen. A stationary electron beam impinging on the melt surface sets up very fast convective cells within the liquid metal, which quite effectively accomplishes this stirring. In vacuum induction melting, the induced field couples to the one to two inch thick graphite crucible rather than the metal inside the crucible. Heat is transferred to the melt by radiation from the graphite, which melts the charge, but doesn't stir the melt.

In a vacuum arc remelt process, there is little clearance between the crucible sidewall and the electrode being melted. It would be difficult to introduce oxygen into the melting zone where it is needed, and if the oxygen were introduced using a tube, the tube, being consumed during melting, would need to be made from uranium.

It may be possible to promote such a reaction using plasma arc melting. This, like EBCHR is a cold hearth process and, while the relatively large beam does not set up convective stirring, the beam is energetic and appreciable mechanical stirring does occur. Safety considerations associated with melting uranium at near-atmospheric pressure using a reactive gas such as oxygen would need to be evaluated.

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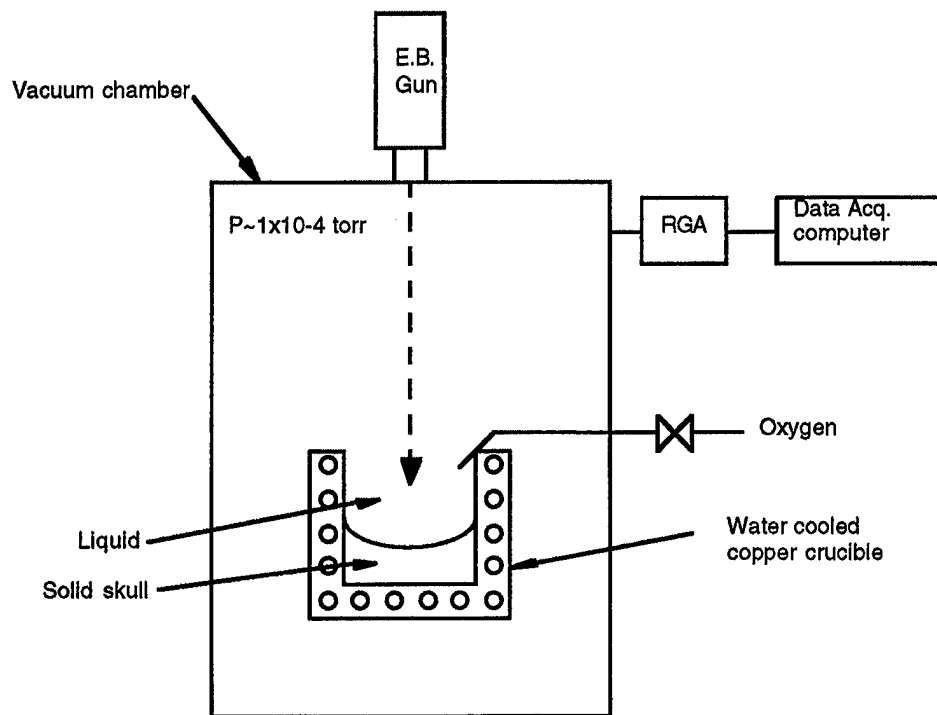


Figure 1: Experimental arrangement

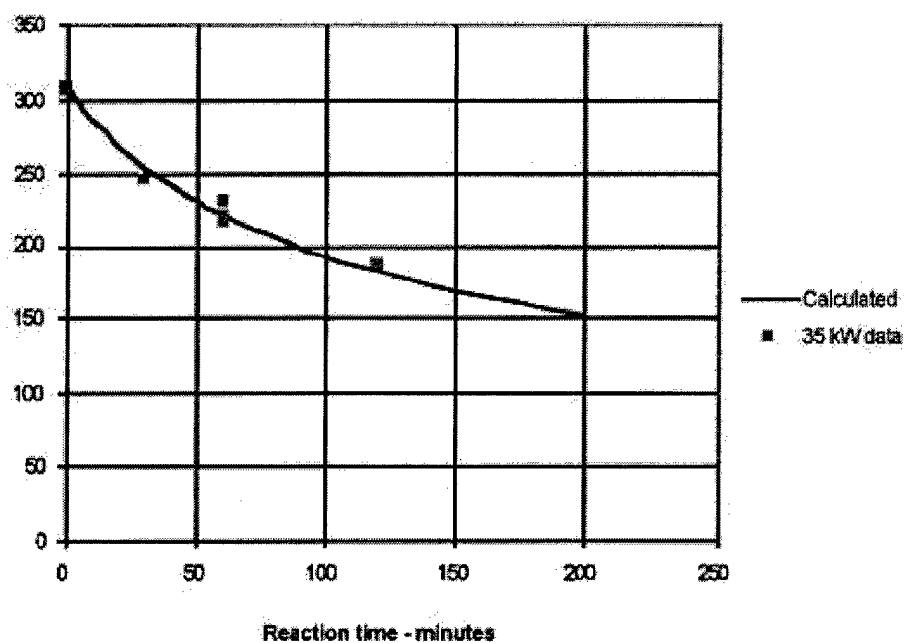


Figure 2: Reaction rate data at 35 kW fit to a third order rate equation

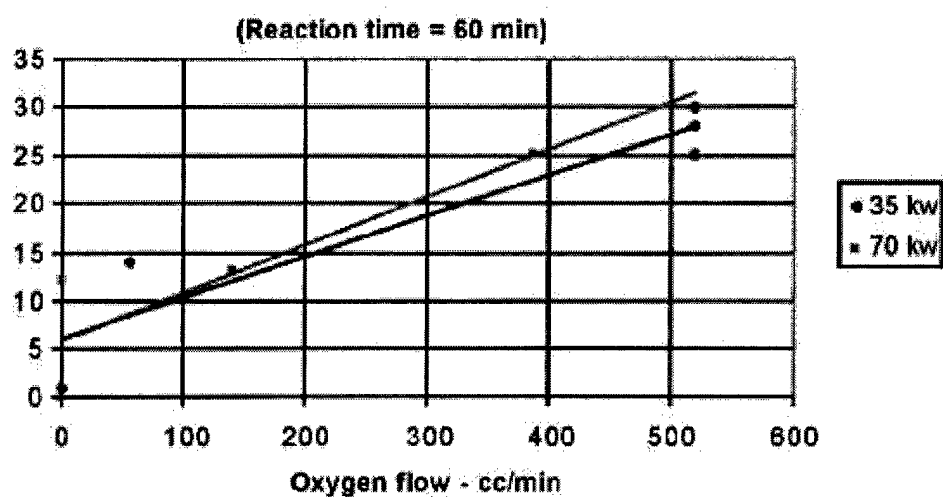


Figure 3: Reaction may be limited by oxygen flow rate

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